Electrospun Silicon Nanowires as Lithium Anodes

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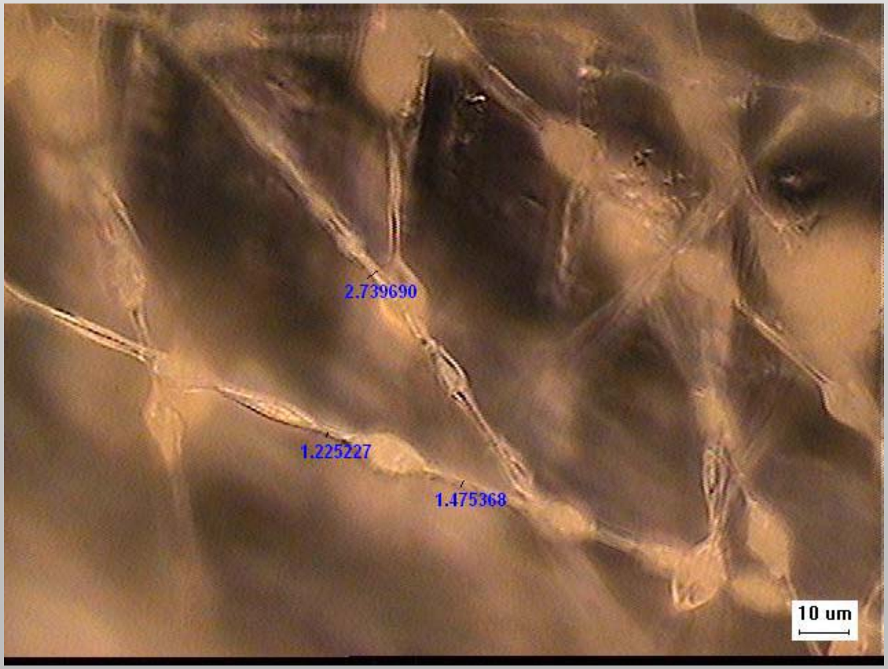
CNSE NDSU Center for Nanoscale Science and Engineering

Pacific Northwest NATIONAL LABORATORY

Outline

1) Si Anodes for LIBs
2) Liquid Silanes – Cyclohexasilane Chemistries
3) Electrospinning a-Si NWs using PMMA as a carrier
4) Half-cell testing
5) Electrospinning *porous* a-Si NWs using QPAC100®
6) Future work



Nano-Si as Li Ion Battery Anode

>10-fold increase in energy density (+)

Li_xC_6 372 mAh/g vs. $Li_{22}Si_5$ ~4200 mAh/g

300% volume expansion during charge (-)

Address mechanical instability by “going nano”

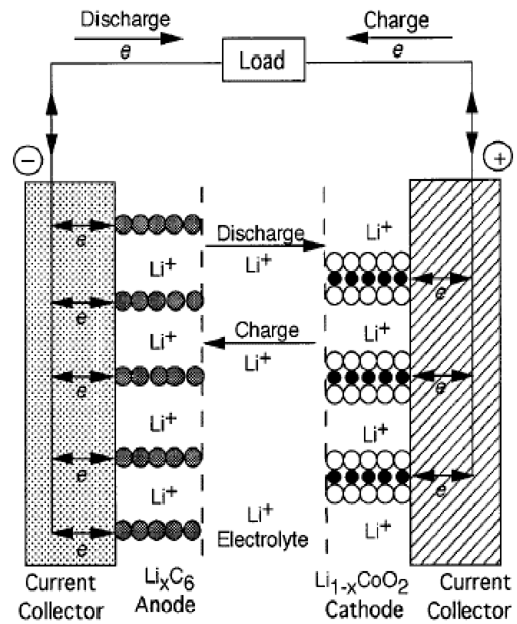


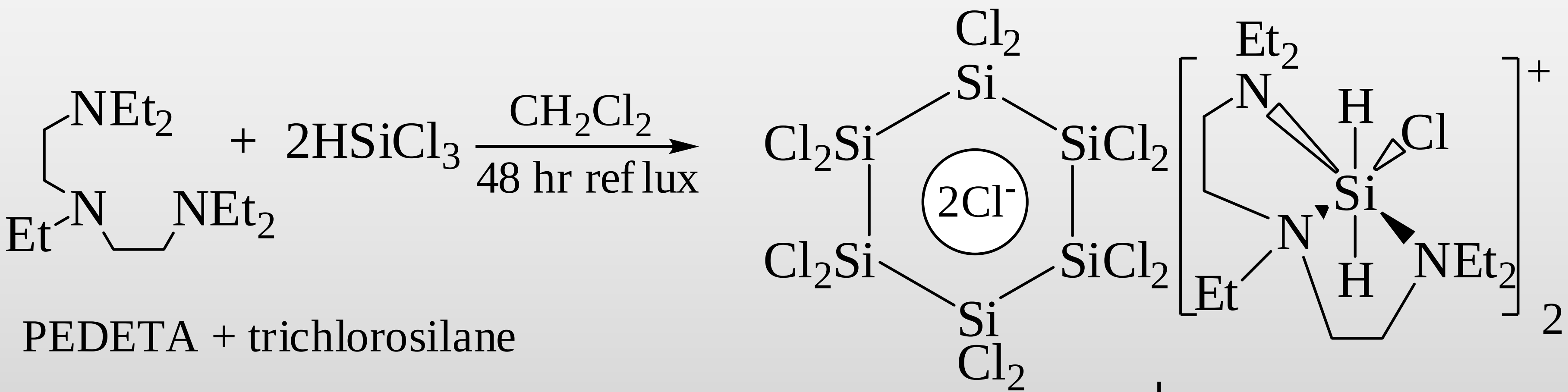
Table 1. A list of Some Si-Based Anode Technologies Being Explored for LIB in PHEV.

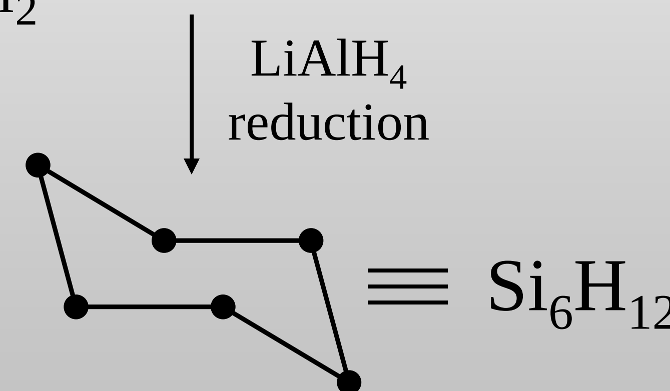
Entity	Anode Type	mAh/g	Benefits/Drawbacks
C. Mellon	Si/C/SWNT’s	1066	Low cycling losses (+) not easily scalable (-)
Montpellier	Ag-Si	1488	High capacity (+); high cost, difficult to scale (-)
Stanford	SiNWs/Au-Si	1000	High capacity (+); high cost, difficult to scale (-)
SUNY-SB	Si/C	500	High carbon content, limited capacity (-)
PNNL	VI-SLS SiNWs	1300	Not easily scalable (-)
U-Pitt	Si/C/PC	1015	High temp process (-)
Kiev Nat’l	Si/C	1235	Scalable process (+); capacity fade (-)
Ulsan Nat’l	Si Nanotubes	3247	Low loss for 200 cycles (+); difficult to scale (-)
A123	C	320	Thermal stability (+); limited capacity (-)
Preliminary at NDSU	E-spun SiNWs	414	Scalable process, low cycling loss and decent capacity for 1st attempt (+); unproven (-)

Figure from Cui, Y. “Nanotechnology-Enabled Memory and Energy Applications”
http://www.caiss.org/docs/Presentation/CAISSDinnerSeminar041708.pdf 04/17/2009

Cyclohexasilane Si_6H_{12} Chemisty

Amine-promoted disproportionation and redistribution: Si-Si bond formation



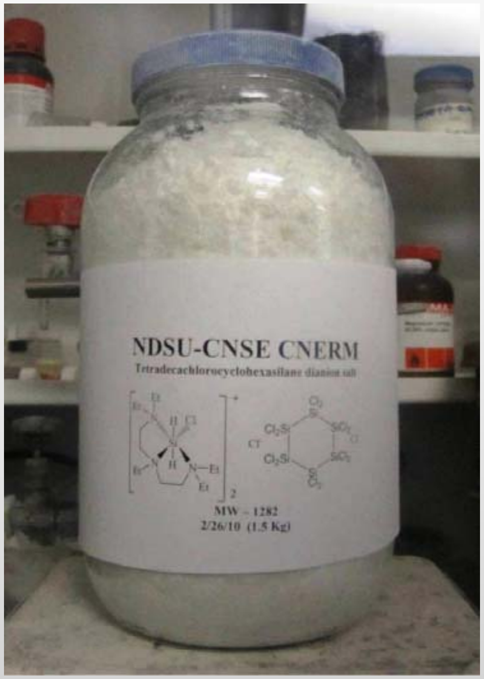


S.-B. Choi, B.-K. Kim, P. Boudjouk, D.G. Grier, *J. Am. Chem. Soc.* **2001,** *123,* 8117.

bp. ~ 220 °C
(80 ° C/10 mTorr)
mp. 18 °C
ρ 0.97 g/mL

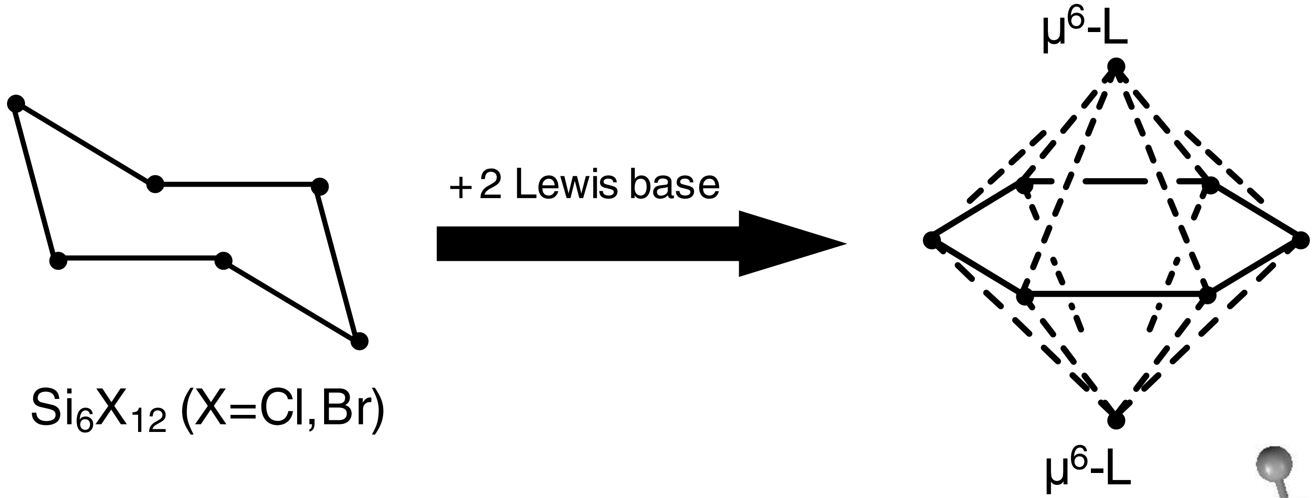
Si_6H_{12} Production at NDSU

- Production level is now 10 g/week.
- 2 kg/day facility envisioned.
- Discussions with several manufacturers of fine chemicals for the semiconductor industry ongoing.

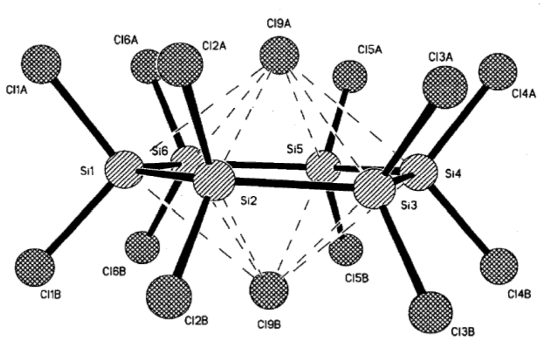


Having Si_6H_{12} in-house offers a competitive advantage

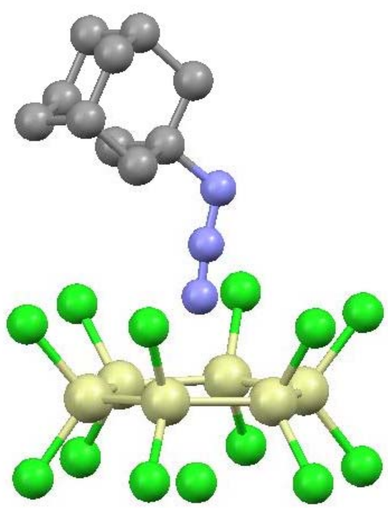
"Inverse Sandwich" Complexes of Perhalocyclohexasilane



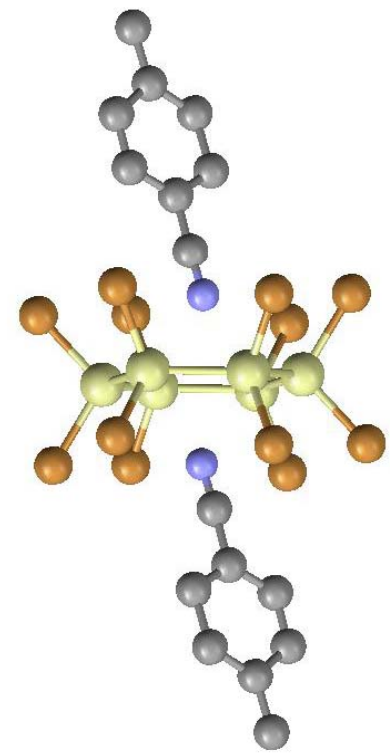
Si_6X_{12} (X=Cl,Br)



Dianion $Si_6Cl_{12}(Cl_2)^{2-}$



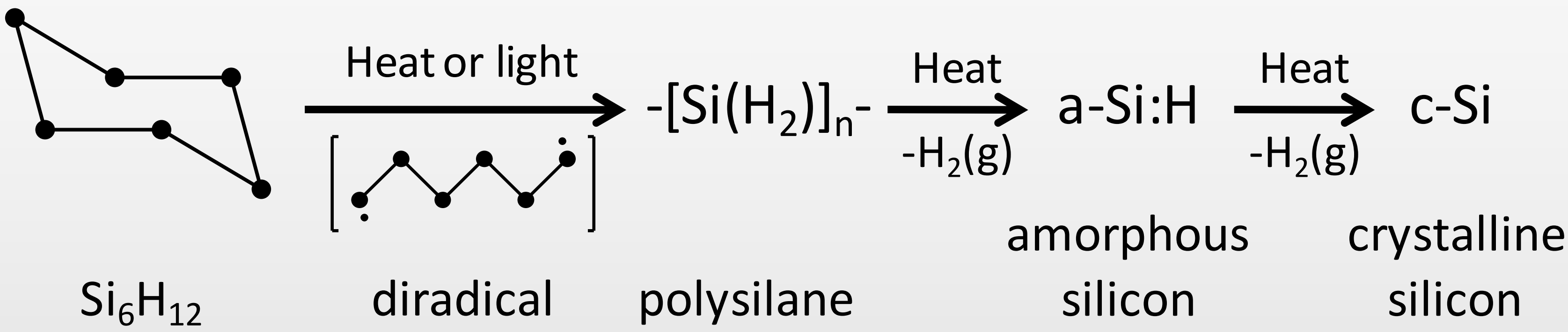
Monoanion $LSi_6Cl_{12}(Cl)^-$



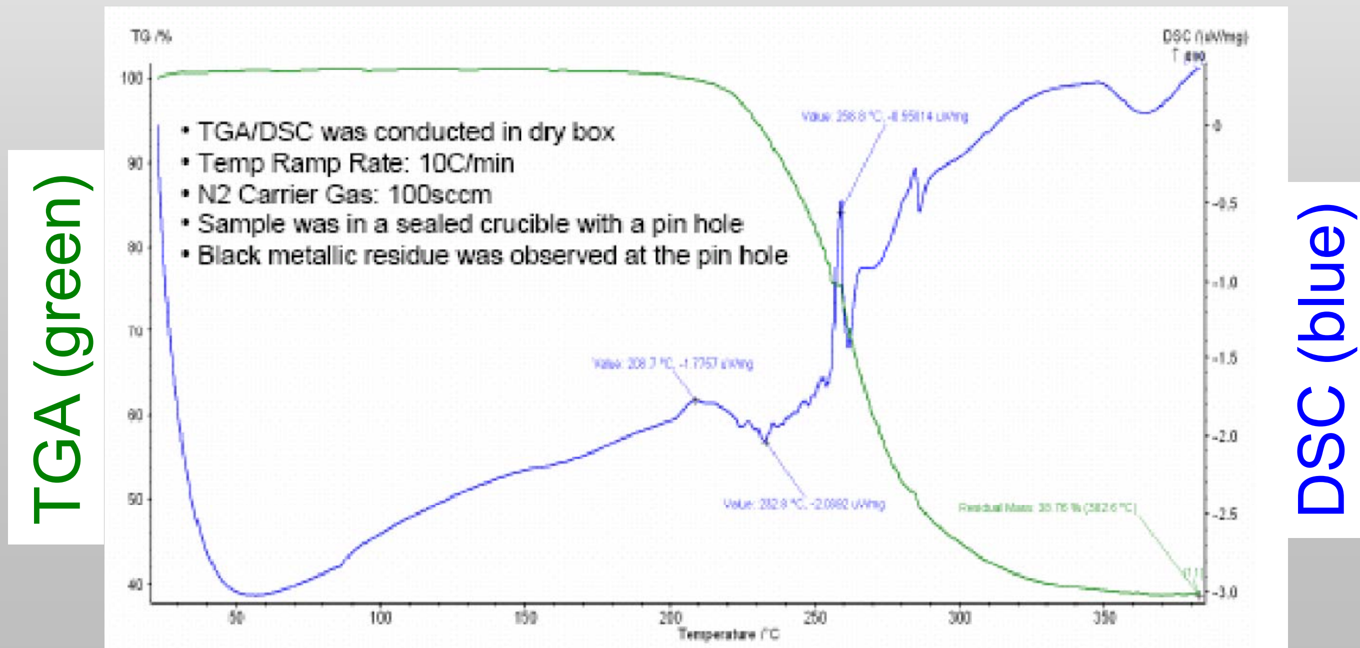
Neutral $L_2Si_6Br_{12}$

Xuliang Dai et al., Organometallics (in revision).

Si_6H_{12} as a Precursor to Si-based Electronic Materials



Si_6H_{12} is Relatively Thermally Stable

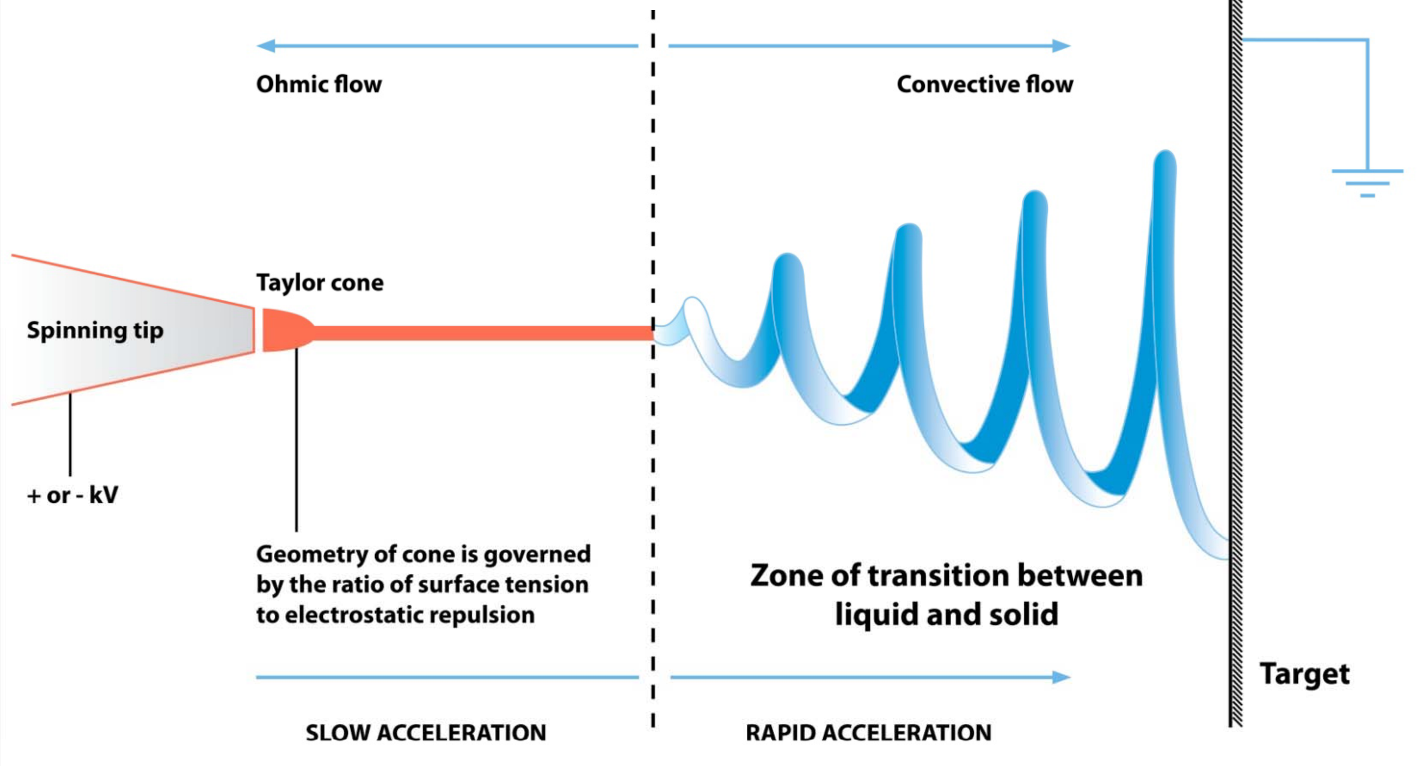


Isothermal TGA at 100 ºC shows no weight change after 12 h

Electrospinning Yields Nanowires

diameters from 1 to 2000 nm

http://upload.wikimedia.org/wikipedia/commons/c/ca/Electrospinning_Diagram.jpg



Synthetic and natural polymers

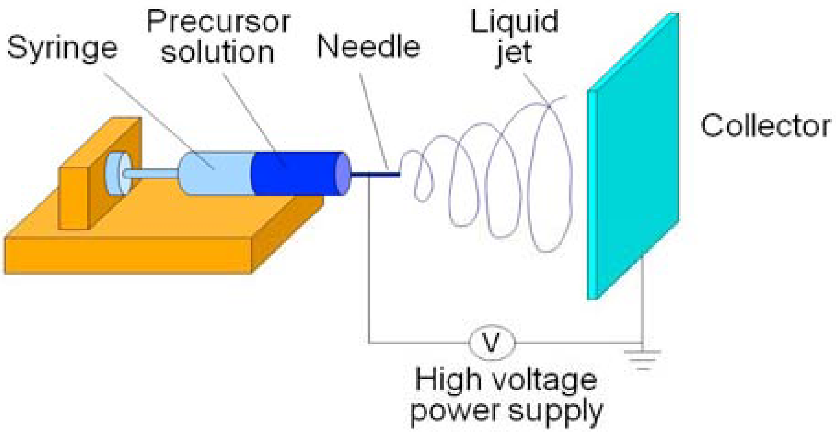
Ceramics

Carbon

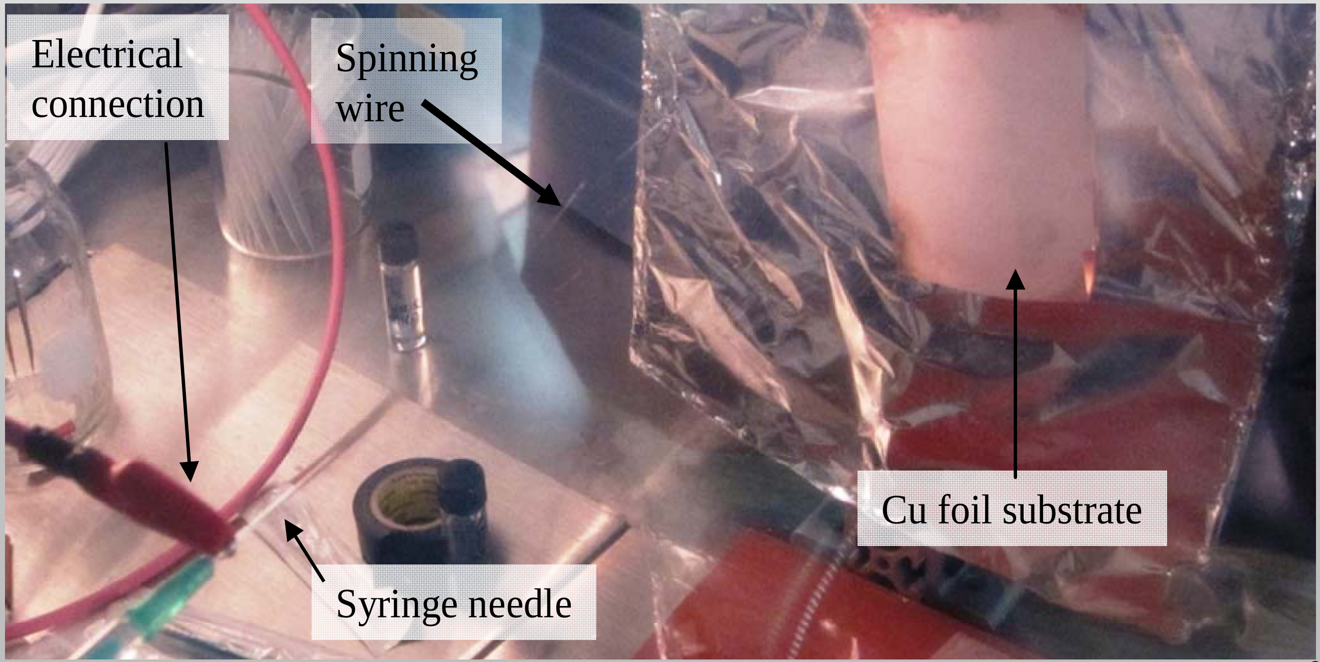
Semiconductor materials

D.H. Reneker, A.L. Yarin, et al, *Adv. Appl. Mech.*, **41**, 43-195 (2007).
D.H. Reneker and A.L. Yarin, *Polymer*, **49**, 2387 (2008).
D. Li and Y. Xia, *Adv. Mater.*, **16**, 1151 (2004).
C. Lai, D.H. Reneker et al.,*Nanotechnology*, **19**, 195303 (2008).
R. Ramaseshan, et al., *J. Appl. Phys.*, **102**, 11101 (2007).

NDSU-CNSE Electrospinning Setup



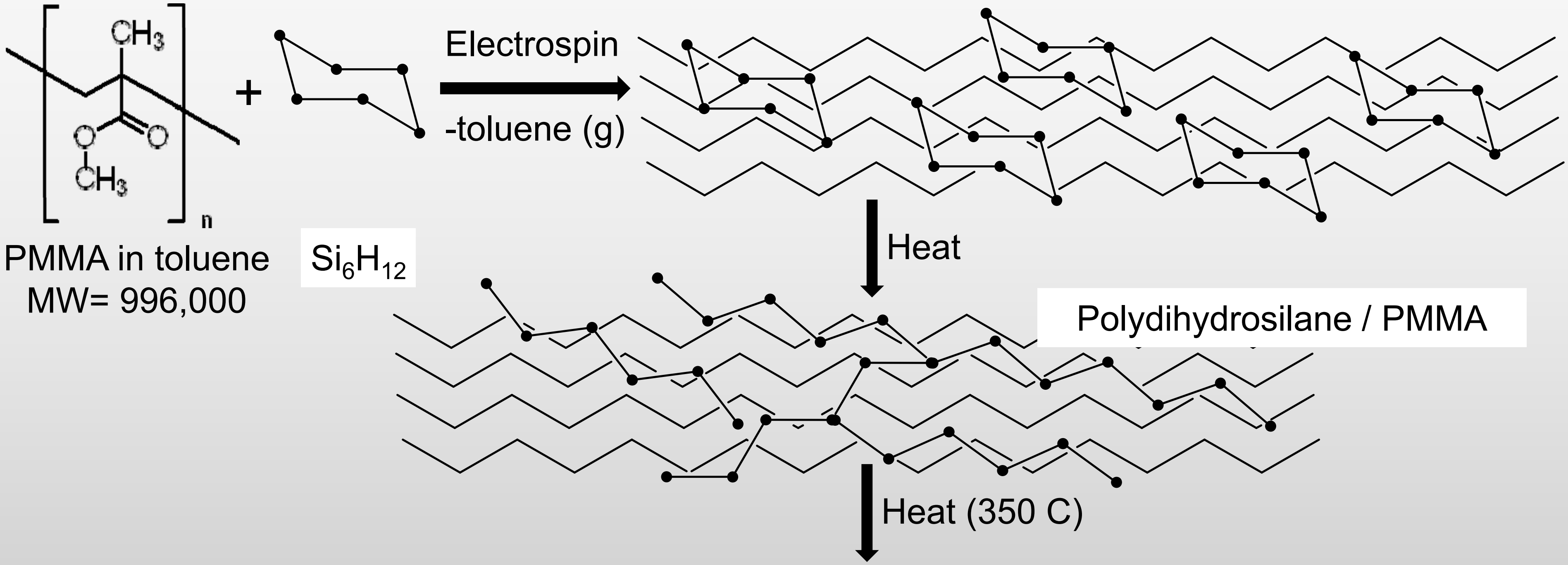
Located inside inert glovebox

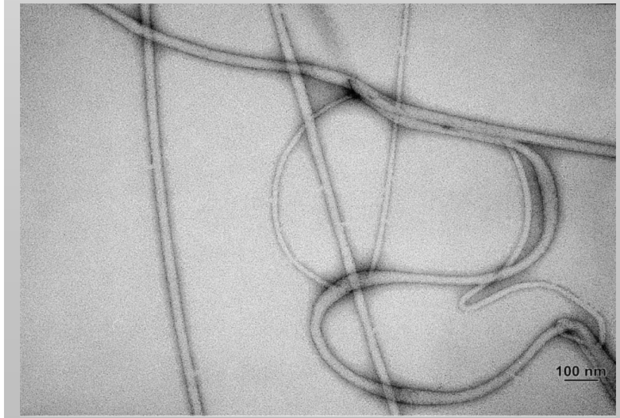


Electrospinning Liquid Silanes

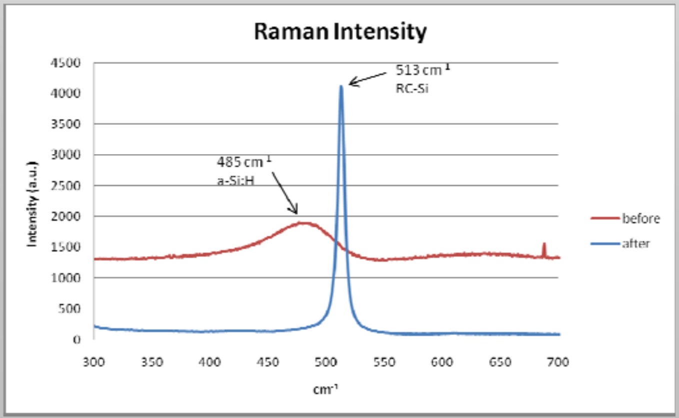
QuickTime Movie

1st Gen Ink. PMMA in Toluene, Add Si_6H_{12}, Electrospin, Thermolysis

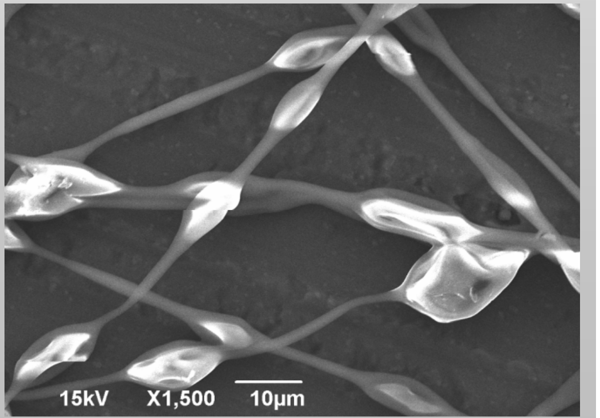




TEM micrograph shows nanowire diameters of 16 to 33 nm



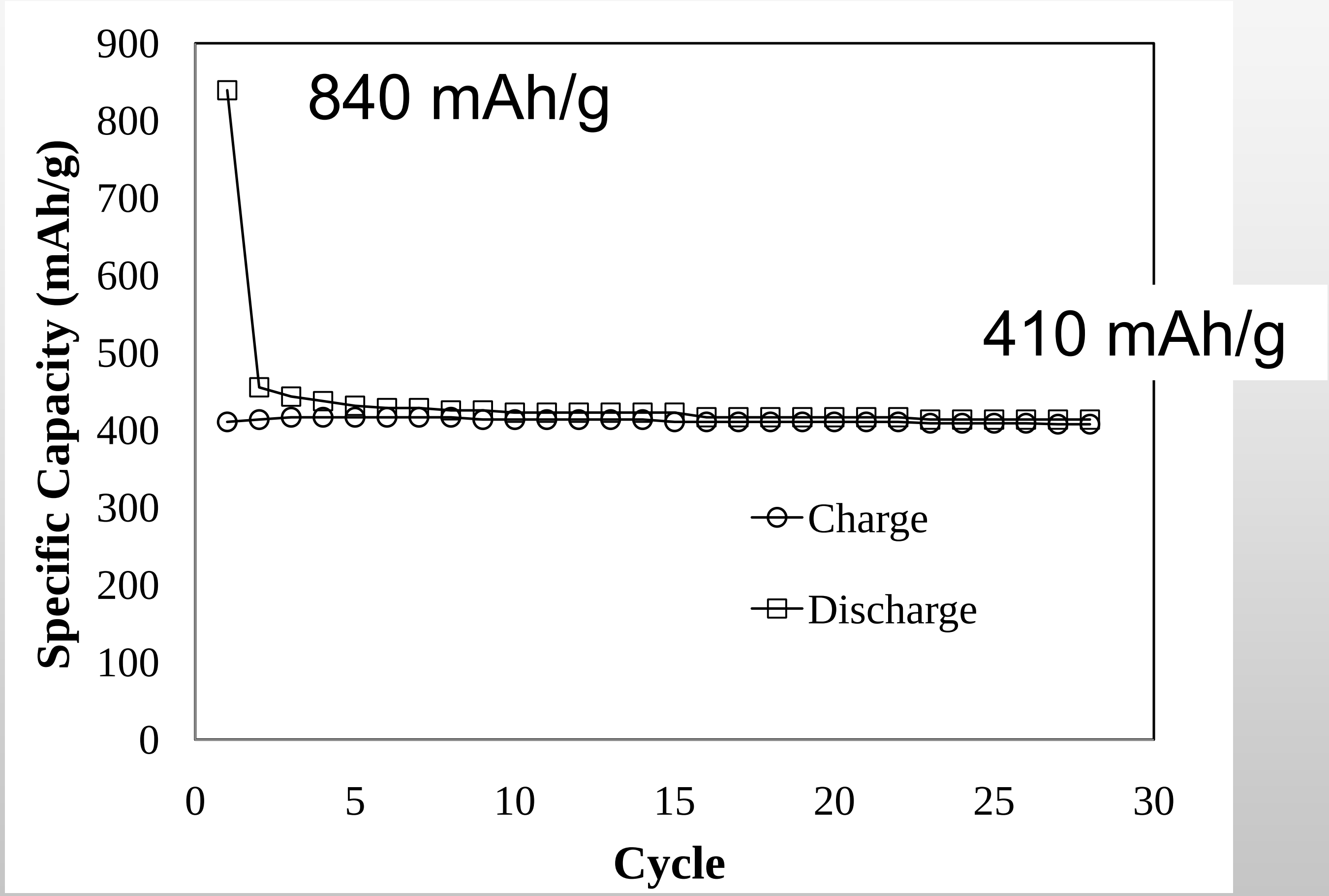
a-Si:H / PMMA
[Note: Raman laser rc-Si]



SEM showing beads – initial formulation

Electrochemical Testing of Li^0/a-SiNW Half-Cell

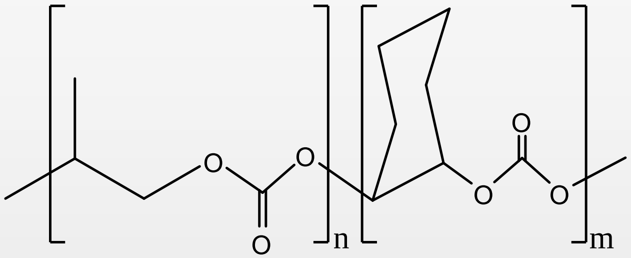
Electrospun a-SiNWs are resilient to cell cycling



specific discharge capacity decreases only 9.2% from 2nd to 30th

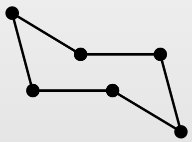
Celgard 2300
1M $LiPF_6$ in (ED:DEC = 1:1)
Cycled between 0.02 and 1.50 V at 100 mA/g

2nd Gen Ink. QPAC100® in Toluene, Add Si_6H_{12}, Electrospin, Thermolysis



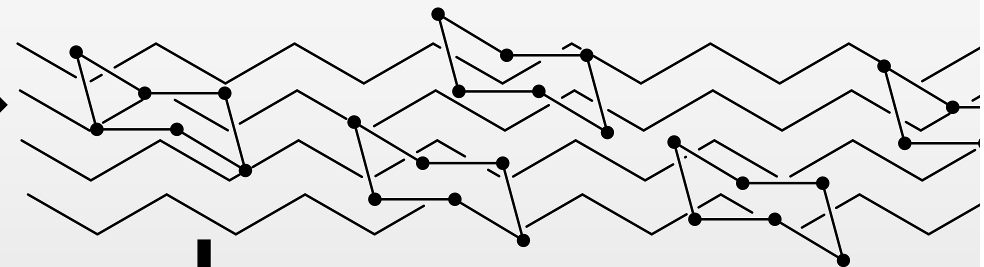
QPAC100®
polypropylene carbonate/
polycyclohexene carbonate
in toluene MW = 660,000

+



Electrospin

-toluene (g)



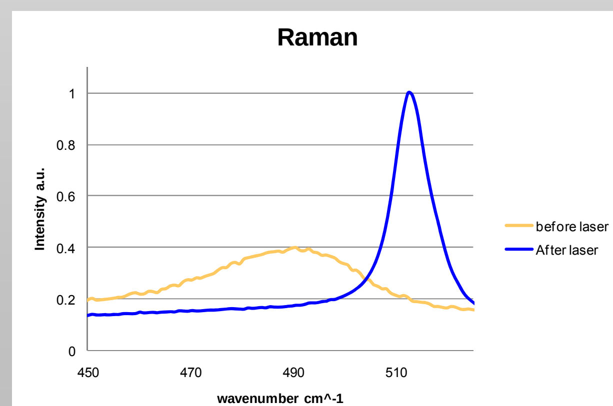
Heat (350 °C/20min)

1) QPAC 100 volatizes

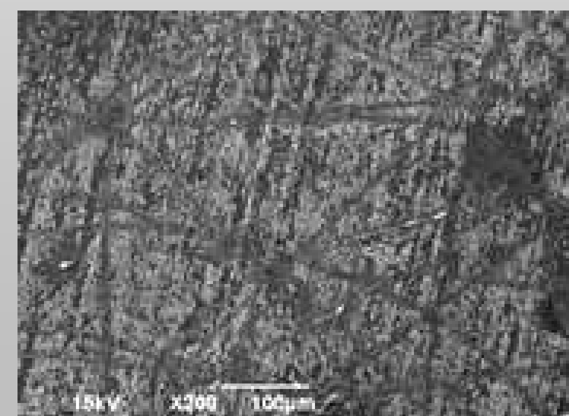
Unpolymerized Si_6H_{12} consolidates on the surface of the substrate

2) Si_6H_{12} transforms to $-[SiH_2]_n-$/a-Si

Optical photograph

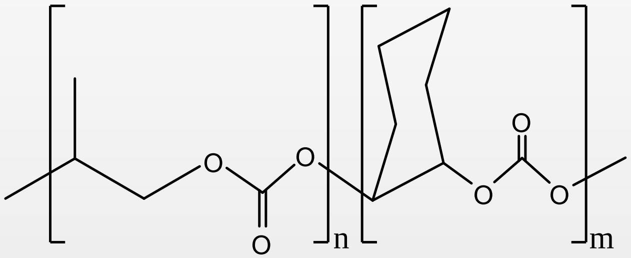


a-Si:H / PMMA
[Note: Raman laser rc-Si]



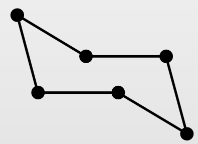
SEM micrograph

2^{nd} Ink'. QPAC100®/Toluene/Si_6H_{12}, E-spin, Laser Treatment, Thermolysis



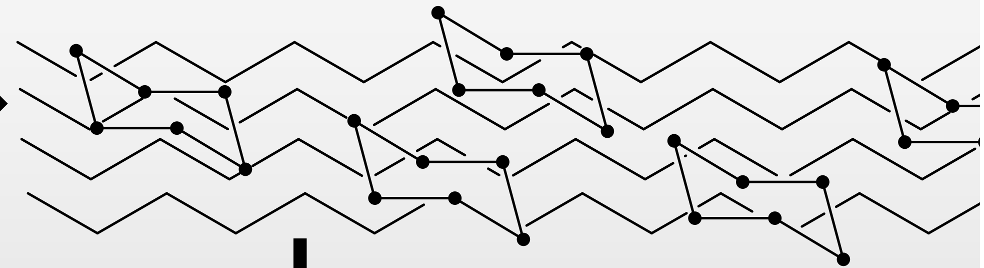
QPAC100®
polypropylene carbonate/
polycyclohexene carbonate
in toluene MW = 660,000

\+



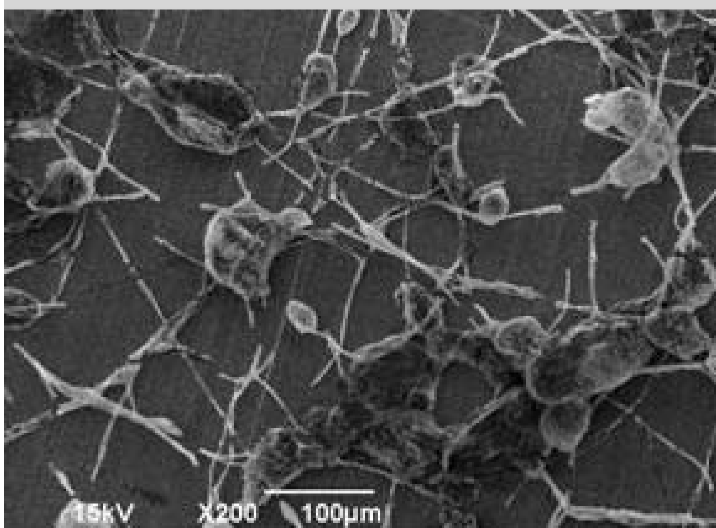
Electrospin

-toluene (g)

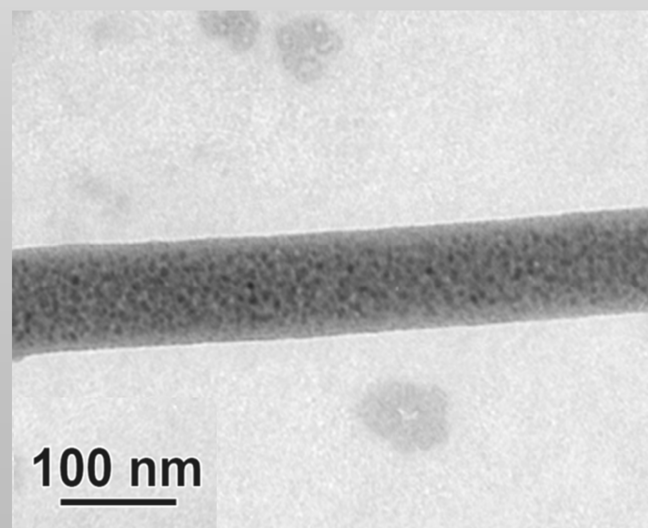


Laser (355 nm @ ~250mW/cm^2)
1) Si_6H_{12} transformed to -$[SiH_2]_n$-

Heat (350 °C/20 min)
2) QPAC 100® volatizes
3) -$[SiH_2]_n$- transformed to a-Si



SEM micrograph



TEM micrograph

Porous
a-Si NWs

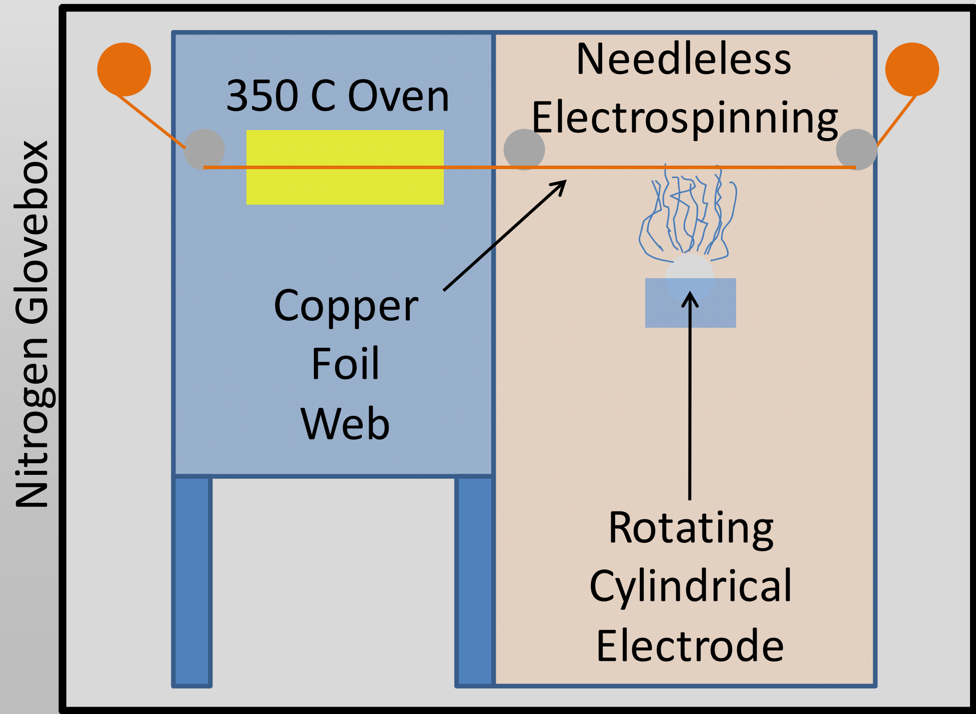
Future Plans

Scaleup Si_6H_{12} production

Refine single-needle electrospinning of Si_6H_{12}

Isolate conducting a-SiNWs using doped inks

Transition to needleless → Cu anode coated with a-Si NWs



A plug-in process for manufacture ?

NanoSpider by ELMARCO

Conclusions

NDSU produces Si_6H_{12} toward pilot scale

Si_6H_{12} can be electospun using a polymer carrier

First a-Si nanowires

First *porous* a-Si nanowires

Initial battery testing similar to crystalline SiNWs

NDSU SiLiSiXErS

★ 2009 All Star Team ★

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Jake Fink	Pooja Vaidya
Chris Braun	Josh Huether
John Lovaasen	Joy Goswami
Chris Olson	Kostia Pokhodnya
Xiangfa Wu	Samy Elangovan
Cody Gette	Kendric Nelson
Iskander Akhatov	Drew Thompson
Justin TT Hoey	Orv Swenson
Larry Pederson	Danielle Vaughn
Kenny Anderson	David Givers
Doug Schulz	Laura Slicer
Kristen Keller	Rob Sailer
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Joe Chapman	Kyle Johnson
Dale Zetocha	Mark Simon
Steve Andrie	Cono Pavone
Phil Boudjouk	Byron Dorgan

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